

SCANDIUM IN AUSTRALIAN COALS AND RELATED MATERIALS

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INTRODUCTION

There is a continued interest in the general chemistry of scandium and in special properties of the metal and its compounds. For example, ferrites containing a small amount of scandium have been used as solid state devices in electronics, and the properties of alloy systems of scandium are being investigated in various laboratories. The metal has a high melting point and a low density. The atomic radius of Sc^{3+} is smaller than that of yttrium and the lanthanide ions, which means that it is not commonly associated with the lanthanide elements, but rather with elements such as iron (as Fe^{2+}). Scandium forms complexes readily.

Despite its widespread occurrence in rocks and minerals, only two definite minerals of scandium have been reported, namely thortveitite $(\text{Sc,Y})_2\cdot 2\text{SiO}_2$ and sterrettite $\text{ScPO}_4\cdot 2\text{H}_2\text{O}$. The scarcity of these and other minerals containing more than 0.1-0.5% Sc has led to interest in sources of scandium, amongst which coal ash, with its wide variety of inorganic constituents, often enriched relative to common rocks and sediments, would seem to be a possibility. The first determinations of scandium in coal were probably those carried out by Goldschmidt and Peters (1), who found 3-300 p.p.m. Sc in 14 samples of ash from bituminous and brown coals (0.1-8 p.p.m. on a coal basis). Deul and Annell (2) found <1 to 100-1000 p.p.m. Sc, with most values between 10 and 100 p.p.m., in 319 samples of low-rank coals from the U.S.A. As part of a general survey of diverse possible sources of scandium in the U.S.A., Ross and Rosenbaum (3) analysed 13 coal-ash samples; these contained 10-30 p.p.m. Sc. The present paper gives the results of an extensive survey of Australian coals and related materials for scandium.

SCANDIUM IN COALS AND VITRAINS

General information on the coal samples is given in Table 1, and the geographical locations of the coalfields are shown in Fig. 1. Details of the emission spectrographic method of analysis are given in the Appendix. It is clear from the results for coals from the Sydney Basin (Table 1) that the overall assessment of the scandium status given by clean-coal composites differs little from that given by whole-seam composites or sub-section samples. Hence, later determinations were usually carried out on clean-coal composites. These results showed that there was a fairly constant concentration (mean 2-4 p.p.m.) in the N.S.W. and Queensland Permian coals. However, slightly higher values were found for the Rosewood-Walloon coals (mean 7 p.p.m.) and the highest values were found for the West Moreton coals (mean 15 p.p.m.). These trends were also apparent in the vitrains (Table 2) which had been separated by flotation, usually at a specific gravity of about 1.3, from samples of most of the seams referred to in Table 1.

Most of the coal ashes had scandium contents close to the clarkie (i.e. the mean abundance of scandium in the earth's crust), which has recently been reassessed (4) as 30 p.p.m. Sc, the main exceptions being some of the Queensland coals. However, apart from the Latrobe Valley brown coals, in which scandium was not detected, the concentrations in most of the coal ashes exceeded the mean content of 10 p.p.m. Sc in sedimentary

rocks (5) and that of 8 p.p.m. Sc for subsoils (6). Shale bands associated with coals in the Sydney Basin had < 3-16, with a mean of 7 p.p.m. Sc. The ashes of the vitrains generally showed distinct enrichment relative to the earth's crust or sedimentary rocks, and the enrichment factors for the former (i.e. the ratio of mean content to the Clarke) varied from about 1.5 to 10. The maximum content of 600 p.p.m. Sc (i.e. 0.09% Sc_2O_3), which was found in samples from three seams in the West Moreton coalfield, exceeded the highest reported value in coal ash of 300 p.p.m. Sc (1).

MODE OF OCCURRENCE OF SCANDIUM

The fact that there is a fairly high concentration of scandium in the vitrains, which contain only traces of clay and other minerals present in the bulk coal, suggests that part of the scandium in the coal is organically bound. Experiments were carried out on six samples of coals from the Sydney Basin in order to ascertain the extent and variability of this association with the coal substance. Each sample was demineralized by treatment with acids to reduce the ash yield to about 1% or less (7). Scandium was determined in the coal before and after demineralization and calculations showed that between 40 and 95% of the scandium in the original coal was organically bound to the coal substance.

As there was also some scandium associated with the mineral matter in the coals, it was decided to ascertain the scandium content of minerals or mineral-rich materials which had been separated from certain coal seams. As will be seen from Table 3, scandium was detected in some siderites, kaolinites and calcites, albeit in low concentrations. On the basis of its atomic radius (0.8\AA) scandium may be expected to be able to replace several cations - for example, Fe^{2+} , Mg^{2+} , Mn^{2+} , Zr^{4+} , Sn^{4+} . The most common host minerals for Sc^{3+} are those high in Fe^{2+} - for example, pyroxenes and biotite - although it is not clear how the substitution is effected, depending as it does on a secondary replacement or rearrangement to balance the otherwise excess positive charge. The presence of scandium in some of the siderites may be the result of a Sc^{3+} - Fe^{2+} replacement. The association of scandium with a limestone, possibly replacing Ca^{2+} (8), may be relevant to the detection of scandium in some of the calcites, where a similar replacement may have occurred. As scandium is unlikely to be substituted in lattice positions or interstitially in kaolinite, its presence in the latter is probably due to adsorption. So far, it has not been possible to separate an apatite from Australian coals, but a subsection sample of a Burrum coal, known to be high in phosphorus present as fluorapatite, contained a lower concentration of scandium than the clean-coal composite of which it was a part. Hence in this case there was no enrichment of scandium as phosphate.

SCANDIUM IN COKE, BOILER DEPOSITS AND FLY-ASH

The results in Table 4 show that scandium, unlike several other trace elements in Australian coals, is not enriched in boiler deposits (9). The concentrations in coke and fly-ash are much the same as in coal ash. As expected, the Queensland cokes had higher scandium contents than those made from N.S.W. coals.

DISCUSSION

The results for scandium in Australian coals indicated a trend from the Latrobe Valley brown coals, in which this element was not detected (i.e. < 0.5 p.p.m.), to the West Moreton bituminous coals with a mean content of 15 p.p.m. Although the latter coals are Triassic, so is Callide coal, which is low in scandium, and, if the one vitrain sample is a guide, then Leigh Creek coals, which are also Triassic, will have similar scandium contents to the N.S.W. and Queensland Permian coals (mean 2-4 p.p.m.). Hence, age is probably not the factor relevant to increase in scandium concentration. It is more likely that the high scandium contents in the West Moreton coals were brought about by adsorption from solutions emanating from source rocks, especially those of

igneous origin, which were able to supply a higher concentration of scandium than was available in other areas. The trivalent scandium ion is readily adsorbed and its small radius and high charge should favour the formation of stable organic complexes, effecting the removal of Sc^{3+} from percolating solutions and its fixation in the coal substance. Although the relative amounts of organically bound scandium vary, there are no minerals associated with Australian coals that are greatly enriched. Some siderites, kaolinites and, to a lesser extent, calcites, showed low scandium contents, and these are the constituents of the mineral matter in coal which contribute scandium. As in the earth's crust, scandium is ubiquitous in Australian coals.

Results for a range of boiler deposits formed during the burning of bituminous and hard brown coals either by grate or pulverized-fuel firing, showed that no enrichment of scandium had occurred. From the point of view of possible use as a source of scandium, the ash from certain coals and vitrains from the West Moreton coalfield merits some consideration. It is difficult to ascertain the present price of scandium, but in 1962 it was quoted as \$2700 per pound of 99% pure Sc_2O_3 (3). However, the desirability of further production of scandium, either from a low-grade, by-product source by solvent extraction (10) or from a higher-grade material, rests on the value assigned to its compounds and alloys in modern technology.

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APPENDIX. METHOD OF ANALYSIS

Gravimetric and spectrophotometric methods, often after separation of a scandium-rich fraction by solvent extraction, cation exchange or paper chromatography, have been reported frequently in the recent literature from the U.S.A., Japan and Russia. However, since satisfactory chemical methods for scandium are usually long and involved, more direct methods, such as neutron activation, X-ray spectrography and emission spectrography, are preferable. For a survey of diverse materials varying widely in scandium content, emission spectrography is well suited, and was used in this investigation.

Samples which were mainly carbonaceous, for example coals and vitrains, were ashed at 800°C prior to analysis, while low-carbon materials, such as boiler deposits and fly-ash, were not ashed. Samples should be about 100 B.S. mesh or less. Two spectrographic techniques were used, brief details of each being as follows:

- (1) When sufficient sample was available, 20 mg, for example, of coal ash was mixed with 20 mg of graphite powder in a small vibratory ball mill, and the mixture was filled into a graphite electrode of the type undercut below the cup to increase the temperature

and thereby assist volatilization. Anode excitation was used in a 9-amp. d.c. arc, with a 4.5-mm arc gap and an exposure time of 2.5-3 min (total burn). A Hilger Automatic Large Quartz (E492) spectrograph was used and the spectra were photographed on Ilford N.50 (Thin Film Half Tone) plates. The final semi-quantitative estimations were made by visual comparison with standard spectrograms. Standards were prepared in a synthetic matrix of similar major-element composition to the samples. The analysis lines used were the ion line at 2552.36\AA and the atom line at 3269.90\AA . The former line is singularly free from interference, apart from platinum which is rarely found, and the latter line can be used in the presence of up to 20% iron and/or 1% zirconium without interference. Each of these lines had a detectability of 10 p.p.m. Sc. The synthetic standards were checked by using them to determine scandium in the synthetic rock sample W-1 (U.S. Geological Survey). The value of 40 p.p.m. Sc obtained is close to most of the values reported; of the 20 values listed by Fryklund and Fleischer (4), 17 were in the range 25-70, with a mean of 40 p.p.m. Sc.

(ii) When only 1-3 mg of sample was available - for example, in the case of some minerals removed from coals - a microspectrographic method was used. The sample was mixed with lithium tetraborate plus graphite powder (usually 2+3+5 mg respectively), and filled into a small graphite electrode. The arcing procedure was the same as before. New standards were prepared, and the detectability was 20 p.p.m. for Sc 2552 and 40 p.p.m. for Sc 3269.

For the determination of scandium in minerals separated from coal (for example, pyrite, siderite and calcite) separate tests were carried out to ascertain the suitability or otherwise of the standards, and corrections were made, if necessary. The standard Sulphide Ore-1 (Canadian Association of Applied Spectroscopy) was found to contain ~20 p.p.m. Sc compared with the recommended value of 25 p.p.m.

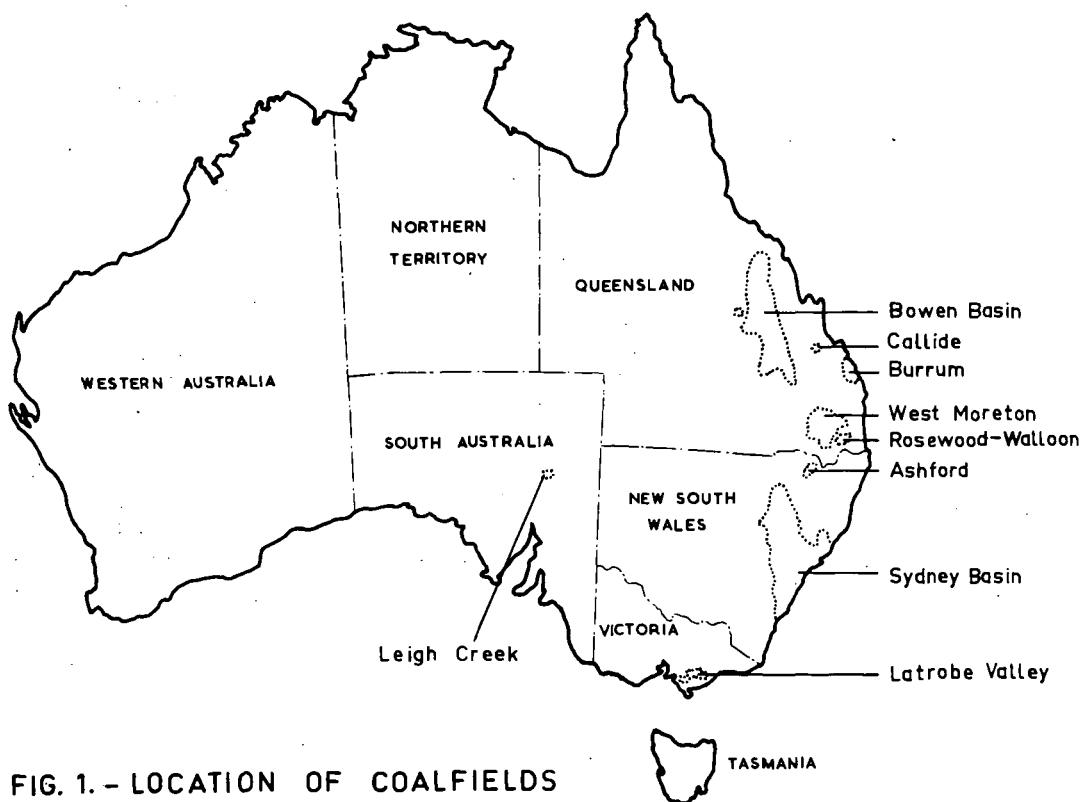


FIG. 1. - LOCATION OF COALFIELDS

TABLE 1. CONTENT OF SCANDIUM IN AUSTRALIAN COALS

Coalfield	Geological Age	No. of Seams Sampled	No. of Samples	p.p.m. Sc			
				On Ash Basis		On Air-dried Basis	
				Range of Values	Mean	Range of Values	Mean
QUEENSLAND (bituminous)							
Callide	Triassic	1	1	-	30	-	4
West Moreton	Triassic	12	24	30-150	60	7-30	15
Rosewood-Walloon	Jurassic	2	7	25-40	35	5-8	7
Burrum	Cretaceous	1	1	-	30	-	3
Bowen Basin	Permian	10	12	10-50	30	1.5-6	3
NEW SOUTH WALES (bituminous)							
Ashford	Permian	1	1	-	20	-	2
Sydney Basin	Permian	20	88	<10-40	20	<0.4-6	2.5
(coal subsection samples)		20	282	<10-100	20	<0.3-10	2.5
(whole-seam composites)		20	26	<10-40	20	<1-6	2.5
VICTORIA (soft brown)							
Latrobe Valley	Tertiary	2	22	-	<10	-	<0.5
(low ash, i.e. < 5%)							
SOUTH AUSTRALIA (hard brown)							
Leigh Creek	Triassic	3	37	*	-	-	-

Note. The above results refer to clean-coal composites, except where otherwise stated.

* Detected in 36 samples, but standards were not available for semi-quantitative estimation.

TABLE 2. CONTENT OF SCANDIUM IN VITRAINS

Coalfield	No. of Samples	p.p.m. Sc			
		On Ash Basis		On Air-dried Basis	
		Range of Values	Mean	Range of Values	Mean
QUEENSLAND					
Callide	1	-	150	-	2.5
West Moreton	27	100-600	350	4-20	10
Rosewood-Walloon	11	60-300	150	2-10	6
Bowen Basin	6	100-150	120	1.5-3	2
NEW SOUTH WALES					
Sydney Basin	20	30-250	100	0.9-7	2.5
SOUTH AUSTRALIA					
Leigh Creek	1	-	40	-	4

TABLE 3. SCANDIUM IN MINERALS OR MINERAL-RICH SAMPLES SEPARATED FROM COALS

Main Constituent	No. of Samples	Brief Details of Samples	p.p.m. Sc
Pyrite	6	4 from Queensland and N.S.W. coals; 2 from Leigh Creek coal	< 20
Siderite	1	From a Sydney Basin coal - 'nodular'	30
Siderite	1	From a West Moreton coal - 'nodular'	40
Siderite	1	From a West Moreton coal - 'massive'	< 15
Siderite	1	From Leigh Creek coal - 'nodular'	< 15
Calcite	3	From Sydney Basin coals	< 10, 10?, ≤10
Secondary carbonate (high in Ca)	1	Cleat filling from a West Moreton coal	40
Gypsum	1	From Leigh Creek coal	< 10
Mudstone	1	From a dirt band in a Sydney Basin coal	10
Bentonite	1	From the roof measures of a Rosewood-Walloon coal	< 10
Kaolinite	1	From a Rosewood-Walloon coal	15
Kaolinite	1	From a Sydney Basin coal	25

TABLE 4. CONTENT OF SCANDIUM IN COKE, BOILER DEPOSITS AND FLY-ASH
(Values are in p.p.m. Sc)

Description of Samples	No. of Samples	Range of Values	Mean	Scandium in Ash of Coal Used
Cokes made from N.S.W. coals	14	25-40	30	-
Cokes made from Queensland coals	3	60-100	80	-
Fused material and deposits from walls of carburettor in water-gas plant	8	-	15	20
Deposits from various parts of a spreader-stoker-fired boiler, burning bituminous coal	32	20-30	25	20
Deposits on super heater tubes of chain-grate stoker fired boiler, burning bituminous coal				
Inner deposits	4	10-20	10	30
Outer deposits	1	-	30	-
Deposits from screen tubes and superheaters of boiler, burning Leigh Creek coal under p.f. conditions	10	<10-20	10	-
Fly-ash from a N.S.W. bituminous coal	21	25-30	30	30
Fly-ash from Leigh Creek coal	2	20, 30	25	-